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Canada Centre for Mineral and Energy Technology
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SHORT-RESIDENCE-TIME (SRT) COAL LIQUEFACTION

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Coal Liquefaction Section

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SHORT-RESIDENCE-TIME (SRT) COAL LIQUEFACTION

by

P. Rahimi*

ABSTRACT

The concept of short residence time (SRT) coal liquefaction is described. The chemistry of conventional coal conversion to liquid fuels in general and short contact time reaction in particular is reviewed. Some experimental results using batch facilities are presented. The batch laboratory reactors used in these studies are ranked against the desired attributes. Finally, based on a critical technical evaluation, a laboratory reactor has been chosen to meet the objectives at CANMET.

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LA LIQUEFACTION DU CHARBON SELON LE PROCEDE SRT (SHORT RESIDENCE TIME) IMPLIQUANT UN COURT TEMPS DE SEJOUR DANS LE REACTEUR.

par

P. Rahimi*

RESUME

Le comcept SRT pour la liquéfaction du charbon est décrit ici. On passe en revue la chimie de la conversion conventionelle de charbon en combustibles liquides, en insistant sur les réactions lors d'un court temps de contact. On présente certains résultats d'expériences effectuées au moyen d'installation en lot. Les réacteurs chimiques de Laboratoire utilisés pour ces expériences ont été comparés face aux qualités désirées. Finalment, après une évaluation technique critique, on a opté pour un réacteur de laboratoire pour atteindre les objectifs du CANMET.

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INTRODUCTION

Short-residence-time (SRT) or short-contact-time (SCT) for coal liquefaction has been defined by Thomas and co-workers (1) as the minimum time at a given temperature required for the complete dissolution of the coal. This time is sufficiently long to convert the coal to preasphaltenes (THF solubles but toluene insolubles), but not long enough so that secondary reactions such as conversion of preasphaltenes to toluene and pentane solubles take place to any significant extent.

Recently, there has been considerable interest in the development of two-stage liquefaction process using SCT coal extraction followed by an upgrading step to produce a distillate fuels (2-6). SCT liquefaction has the potential to liquefy coal at lower cost and higher efficiency than other processes because of lower overall hydrogen consumption due to lower gas make, higher derived liquid yield, and higher output per unit reactor volume. The concept of SCT is derived from the work of Neavel (7) and Whitehurst (8,9) who have reported that coal can be thermally fragmented in a very short time into smaller molecules which are soluble in pyridine.

Neavel showed that within a few minutes at 400°C in a hydrogen donor solvent, coal could be converted to a pyridine-soluble product (see Fig. 1). Under these conditions, little or no external hydrogen was consumed. Further, it was shown that this rapid initial conversion proceeds almost as well in naphthalene, a non-hydrogen donor solvent. The technical importance of this observation is that after a very short time virtually all that is in the reactor is pyridine-soluble product and further conversion is essentially upgrading of the pyridine-soluble product.

The purpose of this report is to carry out a literature survey to identify the existing batch short-contact-time liquefactions units and to select a proper unit to meet objectives at CANMET. The batch short-contact-time coal liquefaction unit, as designed, will be utilized:

(a) to study the mechanism of solvent-coal interaction using heavy oil as solvent;
(b) to study the effect of various gases including CO and H_2S on SCT product yield;
(c) to develop a simple, working kinetic model of SCT liquefaction experimental data;
(d) to determine the role of major process variables on conversion and selectivity.

REACTION MECHANISM OF COAL LIQUEFACTION

Based on postulated chemical structures, the reactive maceral components of coal are highly crosslinked networks consisting of a number of stable cluster units connected by relatively weak linkages. Labile bonds assumed to be affected under liquefaction conditions include:

1. Hydrogen bonds
2. Charge-transfer complexes
3. Ar-CH_2-Ar, Ar$(CH_2)_n$Ar
4. Ar-O-Ar, Ar-S-Ar, R-O-Ar, R-O-R

The weaker bonds such as hydrogen bonds and charge-transfer complexes are usually broken to some extent at temperatures below 250°C. As the temperature increases (400-460°C), other labile bonds are broken yielding reactive fragments.

It is generally believed that coal liquefaction processes involve some sort of hydrogen transfer which is different from classical hydrogenation. Pinchin (10) and Falkum (11) suggested that the initial stage of interaction of coal with molecular hydrogen involved depolymerization of coal to reactive intermediates which either are stabilized by hydrogenation or repolymerize. Berkowitz (12) and Neveal (13) compared coal pyrolysis in which free radicals are formed, with coal liquefaction. The work by Curran, Struck and Gorin (14,15) established the free radical nature of the liquefaction process. The initial step involves fragmentation of the coal structure to produce free radicals which can be stabilized by hydrogen donation from the solvent or by redistribution of hydrogen in the organic matrix (autostabilization) (16). In the absence of donor solvent, the radicals undergo a variety of reactions such as condensation (coke formation), elimination or rearrangement (17). In the autostabilization process there is no net hydrogen transfer from solvent to coal fragments. Most of the hydrogen within the coal matrix is redistributed by the solvent acting as shuttler of hydrogen. The general processes occurring during donor-solvent liquefaction are illustrated in Fig. 2 (18). The intermediate stabilized preasphaltenes are further reduced in molecular weight to asphaltenes, and then to distillable oils and hydrocarbon gases. As preasphaltenes and asphaltenes are further decomposed, the aromaticity of the products can increase due to dehydrogenation of hydroaromatic structures. It has been shown that as asphaltene conversion increases and fewer polar functional groups are present, the remaining by-product asphaltenes are much more aromatic and are hydrogenated at a relatively low rate (19).

Recently, Petrakis, Grandy and Ruberto (20-22) reported in-situ observation of free radicals in coal depolymerization under SRC-II preheater/reactor conditions using electron spin resonance (ESR) spectroscopy. Also, coal has a significant concentration of naturally occurring free radicals. Estimates in the order of 5 to 15 x 10^{18}/g have been made depending on rank. In Fig. 3 the spin concentration is plotted against residence time for Powhatan No. 5 coal at 10.34 MPa H_2 with and without solvents. It can be observed that the coal heated in naphthalene has the highest spin concentration, followed by tetralin and the coal-only case. These results support the expectation that naphthalene would not tend to quench formed free radicals as efficiently as tetralin which is a good hydrogen donor. Further, it has been shown that the spin concentration is dependent on the temperature history of the sample as shown in Fig. 4 (20). Later, Petrakis (21) monitored in-situ the formation of free radicals and showed that temperature is the most significant single process variable that affects free radical concentration. For instance, for Powhatan No. 5 coal there is a 9-fold increase in going from 400 460°C.

THE IMPORTANCE OF SHORT-RESIDENCE-TIME STUDIES

Besides the economical aspects, (i.e. lower hydrogen consumption), SRT coal liquefaction studies had some success in determining the approximate structural building blocks of coal (16-18). It is assumed that the products of the SCT reactions possess significant structural memory of the parent coals. In 2-5 minutes, coal dissolves in the presence of an H-donor solvent. In the absence of an added catalyst only a few bonds are actually broken. Work at Mobil (26), Exxon (27) and Oak Ridge National Laboratory (28) indicates that none of the following reactions takes place in this short reaction time:

1. Hydrogenation of aromatic polycyclic hydrocarbons.
2. Destruction or formation of polycyclic saturated structures.

According to these results, polyaromatic and polycyclic saturates present in coal should be identifiable in the primary liquefaction products.

Many of the chemical functionalities are also stable under these conditions, especially the O, S and N heterocyclic structures. Water formation by phenol dehydration is also minimal. It has been found that in coal liquefaction, the -OH bonded to a monoaromatic ring is quite stable even at long reaction times (up to 90 minutes) in the absence of an added catalyst. However, under the same conditions, dehydroxylation of naphthenic phenols does occur (23).

The degree of aromatic ring condensation in coal liquids was semiquantitatively determined by Whitehurst (26). Further, Farcasiu (23) found that in SCT liquefaction products, the majority of the aromatic rings are like those in benzene and naphthalene. Based on these results it was concluded that in the sub-bituminous and bituminous coals studied in their laboratories and others, the aromatic carbons are not present in significant amounts as highly condensed rings. Liquid-chromatography work (24,29) has shown that up to 40% of the initial products of liquefaction (less than 5 minutes) are of high molecular weight, usually exceeding 2000. These compounds are then rapidly converted to structures of 300 to 900 molecular weight.

Based on the foregoing observations, the advantages and disadvantages of SCT coal liquefaction can be summarized as follows:

1. One of the major disadvantages of conventional coal liquefaction technology is the requirement of large amounts of expensive hydrogen. However, there is no significant hydrogen introduced into the heavy liquids in long contact time thermal processes. In a SCT reaction, the primary liquefaction process takes place utilizing a much smaller quantity of hydrogen.
2. In catalytic hydroliquefaction, separation of coal dissolution step (short-contact-time) from the upgrading stage, allows the utilization of catalysts in more optimal conditions.
3. The products of SCT processes are structurally more representative of the parent coal than of the conventional coal liquefaction products. This can lead to more information regarding the structure and origin of the coal. The study of liquefaction products generated at long residence times could lead to erroneous conclusions regarding the initial structure of the coal. For instance, polarographic (26,29) and ^{13}C, ^{1}H-NMR (24) analysis of the products at various extended reaction times show that the liquefaction products become much more aromatic (due to the conversion of aliphatic carbon into aromatic carbon). Aromatization occurs through dehydrogenation of hydroaromatic structures and rearrangement of polycyclic rings to more stable structures. Thus, if coal were inferred to have similar structures to those of products identified after long reaction time or severe processing conditions, one would conclude that coal is much more aromatic than it really is.
4. In a SCT process less gaseous hydrocarbons and therefore higher yields of liquid products are obtained.

5. One disadvantage of SCT coal liquefaction is with respect to heteroatom removal, especially sulfur. In order to overcome this problem, Longanbach and co-workers (30) suggested a two step process. In the first step, the coal is dissolved at SCT in solvent at relatively low temperature, low pressure and in the absence of hydrogen. In the second step, at higher temperature and pressure, upgrading reactions take place at short contact time and in the presence of hydrogen. The purpose of the second step is to reduce the heteroatom content of the liquid products.

Recently Schiffer and co-workers (2) reported on the development of an integrated two-stage coal liquefaction process. The objective of this effort was to develop a process that converts coal to distillates with low hydrogen consumption by separation of the coal dissolution and hydrocracking reactions. The process comprises three major process steps:

1. First stage coal hydroliquefaction in the SCT mode of operation.
2. Deashing of the coal-derived liquids.
3. Second stage upgrading.

Comparison of the product distribution obtained in two-stage liquefaction of Indiana V coal with the SRC-II and H-coal processes is presented in Table 1. It can be seen that the overall distillate yield and hydrogen consumption efficiency are higher for the two-stage process than for conventional one-stage liquefaction. Furthermore, the sulfur content of the distillate (Table 2) in the two-stage process is comparable to that for the H-coal process and much smaller than for the SRC-II process.

LABORATORY REACTORS FOR SHORT-CONTACT-TIME EXPERIMENTS

Coal liquefaction studies at long residence times are generally carried out in tubular continuous reactors or stirred batch reactors. The correct interpretation of coal conversion kinetics, which, from the early studies, was shown to be very rapid (31-33), depends on how well one is able to monitor and understand the reactions which take place in the initial stages of liquefaction. Since liquefaction using these autoclaves requires long heat-up and cooldown times, it is impossible to study the significant dissolution reactions occurring during heat-up or at very short residence time. Therefore it became necessary to design and operate new systems which are different from conventional liquefaction units.

These units were designed to provide information regarding the kinetics of coal dissolution as well as the chemical nature of the initially formed soluble products.

In more recent studies (34–43), various investigators have devised reactors that overcome the thermal inertia problem and allow measurements to be performed at residence times as short as 0.5 min. Table 3 (44) lists a number of reactors which have been used in these studies. A brief description will be given for each reactor. Specific results obtained in SCT studies using these reactors will be reviewed.

MICROAUTOCLAVE AND TUBING-BOMB REACTORS

The microautoclave is generally made from type 316 stainless steel tubing of variable lengths and diameters. Recently this type of reactor was used by Kleinpeter et al. (45) in SCT studies of coal liquefaction (Fig. 5). In all of these experiments the autoclave was shaken vertically by an electric motor whose rotary motion was converted to reciprocating motion by means of a crank and cross-head linkage. The shaker was supported above a large fluidized sand bath which could be moved up and down rapidly by means of pulleys to immerse or expose the entire autoclave.

In a typical experiment a 30 ml stainless steel microautoclave was charged with coal and solvent. The preheated sand bath was then lifted to immerse the autoclave. As the autoclave approached the desired temperature, small doses of cold sand were added to the bath to keep the autoclave at the prescribed temperature. For a 15 g sample, the heat-up time was 120 seconds to temperatures of 399°C (750°F) to 454°C (850°F). At the end of the prescribed residence time the sand bath was lowered and covered with a transite lid. An empty container was placed under the microautoclave and quickly filled with cold water to quench the autoclave contents to ambient temperature in about 30 seconds. Important results from this short contact time study are summarized below:

1. Indiana V coal was extracted under SCT conditions (426°C, 5 min, 2/1 solvent/coal) to the extent of 85 wt % MAF (THF soluble) without added hydrogen. Hydrogen partial pressure up to 6895 KPa did not improve SCT extraction.
2. At SCT conditions the degree of extraction was found to be independent of solvent hydrogen content over a solvent hydrogen range of 8.6–9.2 wt %.
3. At SCT conditions (5 min), increased temperature did not improve extraction performance.

4. The conversion was independent of residence time (5-30 min) at a solvent/coal ratio of 2/1. However at a solvent/coal ratio of 8/1, conversion increased from 83.3 wt % at 4 min to 90.3 wt % at 30 min.
5. The results of microautoclave extraction were comparable with those for the continuous unit (plug flow) operation at the same residence time and temperature.

A simpler version of microautoclave known as a tubing-bomb reactor has been used in many studies. The bomb consists of pressure-rated 316 type stainless steel tubing closed at one end, and fitted with swagelock fittings, a thermocouple, and pressure readout. The heating system can vary from a metal bath to high temperature heating types. After the reaction is over the tube is inserted in cold water in order to quench the reaction.

Very recently Chakrabartty (46) demonstrated, using a tubing-bomb, that at residence times up to 30 min, the presence of gaseous hydrogen did not improve the product yield from Forestburg coal/tetralin. This result indicated that hydrogen in the gas phase did not participate in the initial stage of coal liquefaction.

A tubing bomb was used by Seth (47) in his study of coal solubilization at short reaction times (10 sec to 4 min) and temperatures between 325°C and 420°C. In this study, the extent of thermal bond cleavage in the coal (Illinois No. 6) was estimated by high temperature spin concentrations using Electron Spin Resonance spectroscopy. Generation of free radicals was related to the concentration of etheric oxygen groups, suggesting that these links, being amongst the weakest bonds in coal, are rapidly cleaved. Seth also studied the role of initially extractable low-molecular weight materials on the short reaction time solubilization of Sahara Mine Illinois coal at 400°C. It was found that the removal of the pyridine extract resulted in a decline in pyridine-solubility on treatment with tetralin at reaction times up to 4 min. These results suggest that the low molecular weight materials act as hydrogen transfer intermediates in coal conversion.

RAPID-INJECTION AUTOCLAVE

In the early studies of rate measurements of coal dissolution, Hill (37) found that the time necessary for the autoclave and mixture to be heated from room temperature to reaction temperature was 1.5-2 hours. When extraction versus time was plotted, it showed that more than 80% of the total possible extraction was obtained before the system reached reaction temperature. Hill (37) and Wiser (42) overcame this problem by using rapid-injection autoclaves (hot charge autoclave).

The equipment consisted of a one-litre autoclave equipped with a magnedrive stirring device with speed control, a water quenching system, an external heater, pressure gauge, liquid and gas sampling lines with a cooling system and a coal injector system as shown in Fig. 6.

In a typical experiment a known amount of solvent (tetralin) was heated to reaction temperature under a helium atmosphere, then the slurry was injected. The operation required approximately two minutes for injection of 50 g coal into 50 cc solvent and produced a temperature decrease of about 8°C. The temperature rapidly returned to the predetermined reaction temperature where it was maintained within 3°C (Fig. 7).

Using this rapid injection autoclave Hill and Wiser came to the following conclusions:

1. the thermal dissolution of coal in tetralin obeys second order kinetics in the initial stage of the reaction, first order in coal and first order in solvent;
2. as the reaction proceeds it becomes increasingly easy to supply fresh solvent to the reaction sites at which time the reaction rate is no longer dependent upon the concentration of the solvent.

Another variation of the hot charge autoclave which was designed and developed by Whitehurst (40-41) is shown in Fig. 8. The system consists of a conventional 300 ml stainless steel autoclave with fixed head, removable lower unit, and magnadrive stirrer; all external connections were through the head. The reactor is equipped with a gas inlet, gas sampling lines and a liquid sampling line. A cooling coil was mounted inside the vessel in direct contact with the contents. A cooling water reservoir pressurized to 1.38 MPa with N_2 was used to give a high coolant flow rate. The injection system consisted of a barrel with a floating piston insert having "O" ring seals. All lines throughout the system were fitted with appropriate vents, rupture discs, drop-out pots, check valves, filters and pressure gauges.

In a typical experiment, 60 g of solvent was placed in the vessel. The unit was sealed, pressurized with 1.38 MPa H_2 and heated by an electrical heater. Once the vessel reached operating temperature, the injection system was sequentially loaded with 15 g solvent, 40 g 1:1 solvent coal slurry, and 5 g solvent. To minimize slurry settling, the time between injector loading and injection was kept as short as possible. When the temperature of the vessel reached about 10°C above the desired temperature, the injector was pressurized and the contents forced into the reactor in about 1 sec. It was shown that the temperature drop of the reactor

when the mixture was injected was about 50-115°C and the recovery to the original temperature was about 0.5-1 min (Fig. 9). To end a run, the heater was removed and simultaneously water flow was started to the cooling coil. The temperature typically dropped about 100°C within 10 sec. The autoclave was then cooled to room temperature and the contents were withdrawn and analyzed in a routine manner.

A series of experiments using West Kentucky and Wyodak coals was carried out using the above reactor under a variety of conditions. Table 4 summarizes the results obtained at 426°C, 6.9-8.9 MPa H_2 in a synthetic solvent (2% 4-picoline; 17% p-cresol; 43% tetralin; 38% 2-methylnaphthalene). The conversion of coal to soluble form occurs very rapidly and varies with the type of coal used. The effect of temperature on the product yield of West Kentucky coal is shown in Table 5. It can be seen that for a 26°C increase in temperature, the coal conversion increased by 20% and SRC yield by 10%.

Effects of solvent type and hydrogen pressure were also studied in the conversion of West Kentucky coal. The results are shown in Table 6. It can be seen that heating the coal in pyridine for either 1.28 or 60 second did not increase coal conversion. Also the use of H_2 without a H-donor solvent (pyridine) results in a small increase in solubility. However, using a H-donor solvent without H_2 at short-contact-time increases the coal conversion considerably (compare Runs No. 2 and 3). Using this system, Whitehurst was able to distinguish between those products which formed in the initial stage of liquefaction and escaped the coal particles, and products which formed in the early stage but remain surrounded by coal particles. By using a filter inside the reactor, it was possible to withdraw products at different intervals. Analysis indicated that SRC yields were lower than what had been obtained from overall reaction. This result indicated that even in well stirred reactors there might be two different reactions taking place inside and outside the coal particles.

Based on the concept of coal liquefaction in two steps, Longanbach and coworkers (30) designed and operated a system which was capable of varying residence time between 0-5 min. This unit which is shown in Fig. 10 consists of three stirred autoclaves. The coal slurry mixture is preheated in autoclave AC-1 to 250°C while autoclave AC-2 is being heated slightly above the reaction temperature while empty. It is claimed that during this heat-up time the mixture is below the temperature (250°C) where significant reaction takes place. The slurry mixture is then transferred to autoclave AC-2. About 0.6-3.4 min. was required for the reaction mixture to reach the reaction temperature. After the desired residence time

the slurry was transferred back to autoclave AC-1 or AC-3 where it was quenched to 250°C using an internal cooling coil. After the gases were vented the slurry was filtered at 250°C.

The main feature of this system is that material balances are more accurate since the material lost in each step is determined unambiguously. Four variables were studied using this unit in order to evaluate the first step of a proposed two-step liquefaction process. These variables were, residence time (0-5 min), H_2 pressure (2.0-12.4 MPa), solvent to coal ratios (2:1 and 3:1) and finally reaction temperature (413-454°C). The coal used in these studies was West Kentucky 9114 and Wilsonville recycle was used as solvent.

Fig. 11 shows THF conversion plotted as a function of reaction time and temperature. It is clear that THF solubles are formed during the heat-up period (0.6-3.5 min). Also, it appears that the lower molecular weight THF solubles may be able to combine in the absence of hydrogen to form higher molecular weight materials which are not soluble in THF (see Fig. 11). Increasing the solvent to coal ratio at short residence time (1 min) did not change the THF soluble materials at 427-441°C. However, the addition of tetralin and the presence of molecular hydrogen in the gas phase increased the THF soluble materials.

Product analysis of short-contact-time studies showed that the easily removable sulfur amounts to about 25% of the total sulfur in the feed coal. This is converted to gas in the first step of liquefaction. The sulfur content of SRC is high and does not meet the standards for SO_2 emissions and should be removed in the presence of hydrogen at higher temperature (second step). It was also found that in the first step only 0.3 wt % hydrogen was transferred from solvent to coal. It has been suggested (30) that the solvent physically stabilizes the coal.

DIFFERENTIAL RECYCLE REACTOR

Another novel reactor that has been used in SCT studies is the differential reactor (48). The development of this reactor is based on a differential conversion and recycle principle. A schematic diagram of a batch differential recycle reactor is shown in Fig. 12. The apparatus is composed of a slurry storage and suspension system, recycle loop, and charge and discharge systems. The recycle loop was composed of pumps, preheater, reactor or dissolver, and quench heat exchange. The slurry storage and suspension system is a 200 ml high pressure autoclave with magnadrive turbine stirrer. Connections through the head consisted of a coal and solvent feed line, a gas sampling and vent line, a return-line from the recycle loop, and a thermocouple for reading and controlling the temperature of the slurry.

The preheater is composed of two halves of a coiled tube heat exchanger (1/8" O.D. x 20' and 0.032 wall thickness). The first half of the preheater was auxiliary for the purpose of fast initial conditioning. The load reduced to a minimum after the system achieved reaction temperature. Fluid temperatures at the exit of the first half of the preheater were kept at 200°C or less during the reaction period to minimize reactions occurring in the preheat section of the system. The quench heat exchanger was composed of two concentric tubes (inner 1/8", outer 1/4" and length of 20') with cooling water flowing through the annular space. The reactor or dissolver itself (Fig. 13) was a tubular down flow type (3/4" O.D., 3/8" I.D. and about 28" in length) with three zone sectional heating. Three thermocouples, in direct contact with the contents at their tips, were used for temperature control and reading or recording. Due to the high mass flux through the reactor compared with the rather small heat transfer area of the reactor, the efficiency of these heaters was not very high. However, it was possible to maintain a uniformity of temperature within approximately 5°C.

In a typical experiment 25 g of pulverized and dried coal (270 mesh) and 225-350 g of solvent were charged into the slurry mixer at a temperature of 400°C (673°K) and system pressure. The slurry was then pumped through the preheater where the heat-up time to reaction temperature was about 2.4 sec. This heat-up took place on each pass through the system. Zero time was chosen as the moment when the reactor temperature reached the run temperature. The nominal hold time in the reactor was approximately 5.7 sec. Finally, the reaction mixture was quenched to 50°C (323°K) in about 3.4 sec.

In order to calculate the reaction time (T) and its relationship to the actual run time (t) the following relationship was applied:

$$wr = W\, dc/dt \qquad (1)$$

r = rate of reaction
c = conversion
w = reactor hold-up (mass)
W = total mass charge less reactor hold-up
t = clock time or run time

From Equation (1):

$$r = dc/d(w/Wt)$$

and also,

$$r = \frac{dc}{dT}$$

Then residence time $$T = (w/W)t \quad (2)$$

It should be mentioned however, that this relationship is only valid for conditions of rapid recycle rate and homogeneous mixing of products. In this unit the slurry was recycled through the system and back to the reservoir at a nominal rate of 14.2 /h; only a differential amount of reaction occurred per pass, and the reservoir was considered perfectly mixed so that the above Equation (2) is considered to be valid.

Two different coals, Hiawatha (Utah) and Kentucky 14 were studied at 400°C and 10.3 MPa H_2 in tetralin. It was shown that both coals were rapidly converted to a full spectrum of products during the initial 5–7 min. The conversion rate then decreased after this period. Further, a new kinetic model of coal dissolution, was developed using this batch recycle system. In an earlier investigation Curran et al. (34) proposed a first order rate model which involved three adjustable parameters to fit their kinetic data. Wiser et al. (43) proposed a second order rate model to fit the kinetic data over a limited conversion range. A new model hybrid model, which is a combination of first order and second order terms was developed to accommodate the kinetic data obtained on the differential batch recycle system. The differential rate expressions are:

$$dx/dt = k_1 (X_{max} - X) + k_2 (X_{max} - X)^2 \quad (3)$$

or

$$dx^*/dt = k_1 (1 - X^*) + k_2 (1 - X^*)^2 \quad (4)$$

Integration of Equation (4) with boundary conditions of $X^* = 0$ and $X^* = 1$ at $t = 0$ and $t =$ infinity yields:

$$1 - X^* = 1 - X/X_{max} = \frac{k_1 \exp(- k_1 t)}{k_1 + k_2 (1 - \exp(- k_1 t))} \quad (5)$$

Where X is the fractional conversion at time t, X_{max} is potential maximum conversion, $X^* = X/X_{max}$ which is a fractional conversion normalized to the potential maximum conversion, and k_1, k_2 are apparent rate constants for first and second rate terms respectively.

Typical conversion-time data based on benzene solubility of the products at 350, 375 and 400°C is shown in Fig. 14. It can be seen that the experimental data fit the data calculated using the above model. The activation energy obtained from these kinetic studies for Hiawatha coal was calculated to be 142.6 KJ/mole (34.1 k cal/mole) for the first order rate constant and 84.5 KJ/mole (20.2 k cal/

mole) for the second order rate constant (Fig. 15). The magnitudes of these values are rather small for a chemical process. It may be possible that the medium magnitude may be a combination of physical and chemical processes with an apparent low enthalpy for the chemical reaction and a high enthalpy for the physical process.

EVALUATION OF LABORATORY REACTORS

Choosing the type of laboratory reactor for evaluating process kinetics is an important step in an industrial process development program. A bad choice would result in inaccurate data, which would scale-up erroneously, leading to a disastrous commercial design. In the following the advantages and disadvantages of the different reactors which have been used in SCT studies of coal liquefaction are reviewed. As is typical of many complex industrial reaction systems, no one reactor turns out to be ideal from all points of view.

NATURE OF REACTING SYSTEM

As mentioned earlier, a typical coal-liquefaction unit consists of a transfer-line, slurry preheater and reactor. The temperature in the preheater is usually close to the desired reactor inlet temperature. It is in this stage that dissolution of a large fraction of coal takes place, producing coal liquids and gaseous products. The rate of coal dissolution has been demonstrated to be extremely rapid and depends on coal type, temperature, pressure, and nature of solvent, but it is generally found to be independent of particle size (as long as particle size is below approximately 100-200 μm).

With gas, liquids and solids under reaction conditions, three-phase flow exists. There may be mass transfer problems. The particular system chosen is either exothermic or endothermic at the initial stage of the reaction, which means there will be difficulty in obtaining isothermal data. Complex feedstocks consisting of many different reacting species will present analysis and sampling problems. Furthermore, the rapid rate of dissolution of coal in the early stage will lead to difficulties in measuring the intrinsic kinetics.

Once the nature of our reaction system is known, the important attributes of the laboratory reactor should be considered. The following list of features are considered to be important in SCT studies of coal liquefaction:

1. Injection system.
2. Sampling and analysis of product composition.

3. Reactor size.
4. Residence-time measurement.
5. Isothermality.
6. Operability.
7. Reproducibility.
8. Construction difficulties and costs.

In the following, various potential laboratory reactors are evaluated in terms of the key attributes for SCT coal liquefaction studies. An overall evaluation of three different reactor types is shown in Table 7.

MICROAUTOCLAVE REACTOR

While the microautoclave is one of the easiest reactors to build and operate, it has several disadvantages. The main drawback is reactor size. The number and the size of reactors are limited by the working volume of the sand bath which is the usual heating source. Considering the type and the number of analyses which should be carried out on the small amount of products obtained in this type of reactor, care must be taken in order to obtain good material balances and in the interpretation of the results. This problem is even more pronounced at low conversion. If good shaking is provided, the mixture would be homogeneous and isothermality will be obtained throughout the reactor. There might be a problem of mass transfer, however, if shaking of the reactor is not sufficient (48). The accuracy of the residence time measurement in this reactor depends on how well the components are mixed at the time of reaction, the time to heat the reactor to reaction temperature and how rapid is the quenching of the reaction mixture. Liquid sampling from the microautoclave during reaction is cumbersome, if not impossible.

RAPID INJECTION AUTOCLAVE

A number of different rapid-injection autoclaves have been designed for SCT studies. The operation of these autoclaves is more difficult than operation of microautoclaves but has two distinct advantages: the capability of maintaining constant pressure during reaction by adding make-up hydrogen, and the ability to measure gaseous-hydrogen consumption and gaseous products. Further, liquid products can be withdrawn from the liquid sampling line during the reaction. The most difficult part of the operation is the injection of coal into the reactor. This is usually done with the help of the solvent being used in the reaction or in another variation, dry coal is injected using some of the hydrogen charge. Reactor size can vary depending on the type of experiment. The quantity of products obtained is

usually large enough to carry out all the required analyses. Another good feature of stirred autoclaves is that the contents of the vessel are well mixed at all times so that accurate residence time and good isothermality can usually be obtained. Finally, the reproducibility of the experiments carried out in these reactors is good.

DIFFERENTIAL RECYCLE REACTOR

One of the major advantages of this system is that the products can be sampled at various times during the reaction, thus allowing several measurements to be made during a single experiment. The main problem with differential recycle reactors is in the analysis of the product composition. By its nature, the differential reactor gives a small incremental conversion which can be difficult to measure for a complex multicomponent system. This limitation, of course, will depend strongly on the nature of the analysis required. It is usually assumed that the slurry is perfectly mixed throughout the system. However any channelling in a differential recycle reactor would be fatal and Equation (5) would no longer be valid for measuring residence times. Due to the small conversion, heat release will be relatively small and if there is homogeneous mixing of products, it is assumed that the reactor is operating under isothermal conditions. Although differential recycle reactors seem to be attractive in some aspects, there is a drawback in terms of operability of the unit. The coal slurry needs to be pumped and recycled from slurry mixer to the preheater, dissolver and quencher (Fig. 12). Any plugging or pumping problems in the unit will be fatal and will result in termination of the experiment.

SUMMARY

The choice of a laboratory reactor to study short-contact-time coal liquefaction is not a simple one. Although it was tried to rank the various reactors against the desired attributes, the final choice is likely to be a compromise. From what is presented in Table 7, it seems that hot charge or rapid injection autoclave is the reactor most suitable for SCT studies, as their limitations have been identified and can be accounted for in the subsequent experimental program.

Based on SCT studies, the concept of integrated two-stage coal liquefaction has been developed. In this process hydroliquefaction and upgrading reactions are separated which permits each to be run at its optimum conditions resulting in higher distillate yield and higher hydrogen utilization efficiency.

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TABLE 1 - Product Distribution of Two-Stage vs. Single Stage Liquefaction of Indiana V Coal

Yields, wt % of MAF coal	SRC-II	H-Coal	Two-Stage
C_1-C_4 Gases	18.8	14.8	5.1
Naphtha	11.6	18.6	7.4
Mid Distillate	20.3	24.7	38.8
Heavy Distillate	9.0	5.3	9.0
Hydrogen Added, wt % of MAF Coal	5.0	5.5	4.67
Distillate Yield, wt % of MAF Coal	40.9	48.6	55.2
Hydrogen Consumption Efficiency (# Distillate/# Hydrogen Added)*	8.2	8.8	11.8

* - # unit weight

TABLE 2 - Distillate Sulfur of Two-Stage vs. Single Stage Liquefaction of Indiana V Coal

Sulphur Concentration (wt %)	SRC-II	H-Coal	Two-Stage
Naphtha	0.19	0.06	0.06
Mid Distillate	0.22	0.08	0.07
Heavy Distillate	0.38	0.08	0.09

TABLE 3 - Short-Residence-Time Reactors for Studying Coal Dissolution*

Reactor Type	Reactor Dimensions, Description	Volume, cm^3	Heatup/Cooldown Times	Charge
Microautoclave (34,35) and fluidized sand bath	1.59 cm i.d. x 15.24 cm Vertical agitation 2300 cpm	30	2.5 min/30 sec	2 g coal, 4-8 cm^3 solvent
Tubing bomb (39) and fluidized sand bath	7.6 mm i.d. x 17.8 cm Vertical Agitation 40 cpm	8	28 sec/10 sec	1.5 g coal, 3 g solvent
Rapid-injection (40, 35) Autoclave	Standard stirred autoclave Agitation 1200 rpm	300	0.5-1 min/10 sec	Injector: 20 g coal, 40 g solvent Vessel: 60 g solvent
Same (40)	1.11 cm i.d. x 15.25 cm No agitation	16	Similar to above	Injector: 1 g coal or 1 g coal, 1 g solvent Vessel: 10^3 cm solvent
Same (43)	Standard stirred autoclave Agitation 1500 rpm	1000	2 min/ Sampled during tests	Injector: 50 g coal, 50 cm^3 solvent Vessel: 450 cm^3 solvent
Differential-Recycle Reactor	Preheater: 1.5 mm i.d. x 6.0 m Reactor: 9.5 mm i.d. x 43.8 cm Quench: 1.5 mm i.d. x 6.1 m Reservoir	11.4 31.2 14.6 200	2.4 sec/3.4 sec	25 g coal, 225-350 g solvent

* Taken from Reference 44

TABLE 4 - Effect of Residence Time on Liquefaction of West Kentucky Coal

Run No.	1	2	3	4	5
Time (min)	0.00	0.5	1.30	40.00	417.00
% Sol. (pyridine)	28.0	50.0	78.20	92.52	96.10
SRC Yield	28.0	46.80	76.10	80.11	61.05

Effect of Residence Time on Liquefaction of Wyodak Coal

Run No.	1	2	3
Time (min)	0.00	1.30	137.50
% Sol. (pyridine)	11.50	45.97	91.52
SRC Yield	11.50	38.53	70.03

TABLE 5 - Effect of Temperature on Liquefaction of West Kentucky Coal

Run No.		1	2
Solvent		Synth	Synth
Temperature,	°C	426	452
Pressure, H_2	MPa	9.3	6.9
Residence Time,	min	0.50	0.50
MAF Conversion,	wt %	50.00	70.07
SRC,	wt %	46.78	56.31

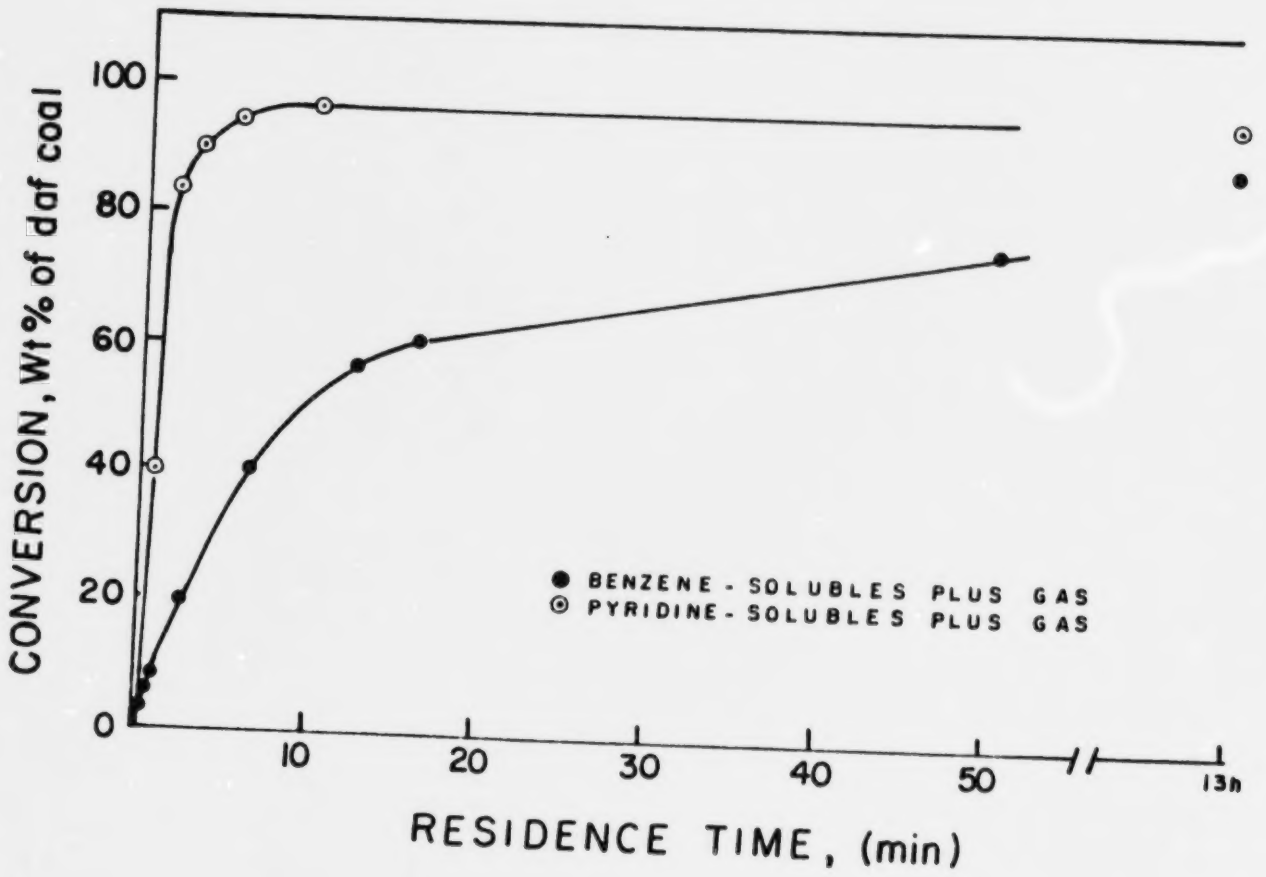
TABLE 6 - Effect of Solvent and Hydrogen in the Conversion of West Kentucky Coal

Run No.		1	2	3	4	5	6
Solvent		Synth	Synth	Pyrd	Pyrd	Synth	Pyrd
Temperature,	°C	426	426	426	426	425	424
Pressure, H_2,	MPa	0.00	8.9	0.00	5.5	8.0	0.00
Residence Time,	min	1.28	1.30	1.28	1.18	40.0	60.0
MAF Conversion,	wt %	65.36	78.20	30.95	40.13	92.52	29.78
SRC,	wt %	58.58	76.12	26.00	28.56	80.11	19.67
H_2 Consumption	g/100 g coal	0.29	0.34	0.00	0.00	0.89	0.00

TABLE 7 - Evaluation of Laboratory Reactors

Feature	Microautoclave		Rapid Injection Autoclave		Differential Recycle Reactor	
	Comments	Rating	Comments	Rating	Comments	Rating
Injection System	Not Required	-	Getting all the material (coal) or or slurry into the reactor might be a problem	fair-good	Not Required	-
Sampling and Analysis of Product Composition	No sampling possible during the reaction	poor	Normal problems	good	Can be difficult at low conversion	poor-fair
Reactor Size	Small	poor-fair	Can be any size	good	Limited	fair
Residence Time Measurements	Known if good mixing and rapid quenching	fair-good	Accurately known if good mixing, rapid heating and quenching	fair-good	Channelling may cause problem	fair-good
Isothermality	Problem if not well mixed	fair	well mixed	good	low heat release	fair-good
Reproducibility	-	poor	-	good	-	fair
Operability	simple	fair-good	Normal problem with injection system	fair-good	Slurry pumping may cause a problem	fair
Construction Difficulty and Cost	Simple	good	More complex than microautoclave	fair-good	Requires recirculating pump	fair-poor

Figure 1 : CUMULATIVE CONVERSION OF COAL IN TETRALIN AT 400°C (after Neavel, 7.)



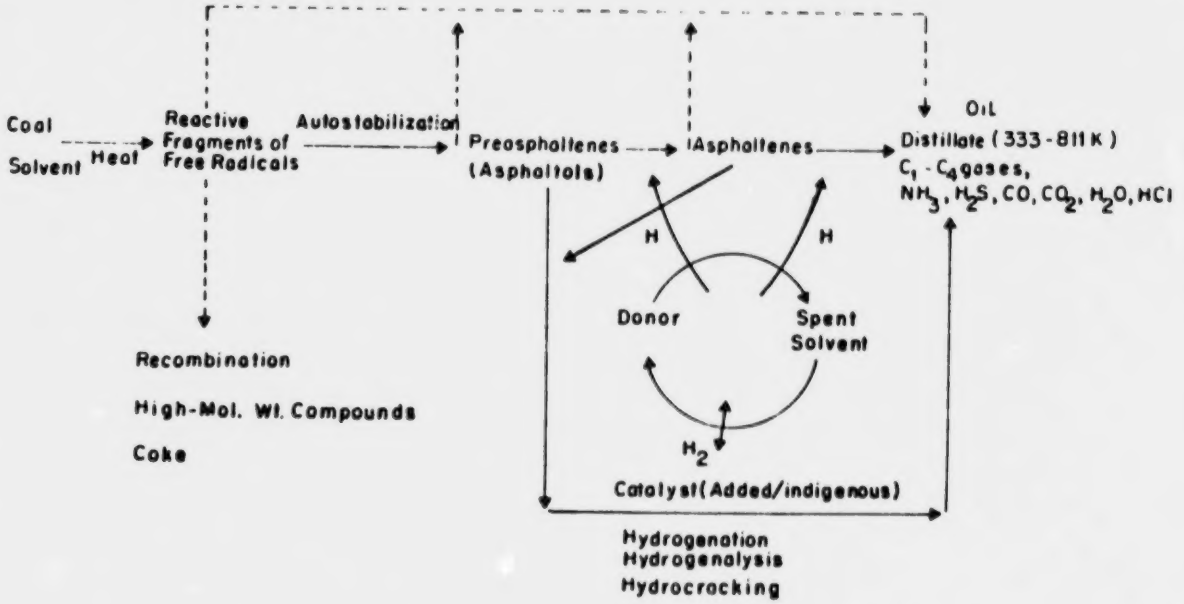


FIGURE 2: General Reaction Paths Occurring During Donor-Solvent Coal Liquefaction (Ref. 18)

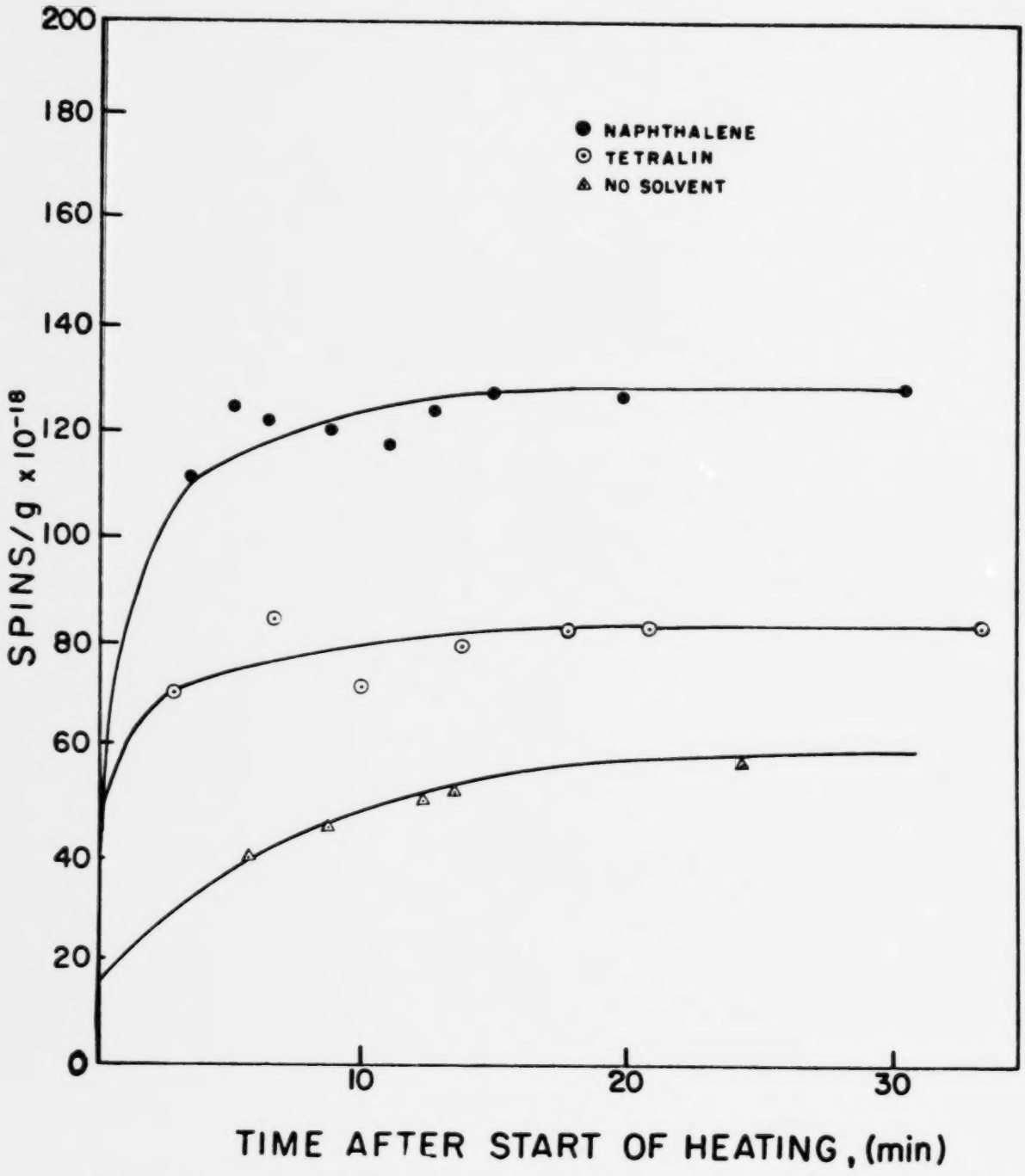


FIGURE 3: Composite of Powhatan No. 5 Coal and H_2 with Naphthalene, Tetralin and No Solvent. Spin Concentration vs. Time. Temperature at T = 0, ~20°C; Temperature at T > 0, 450°C; ●, naphthalene; ⊙, tetraline; ▲, No Solvent (Ref. 21)

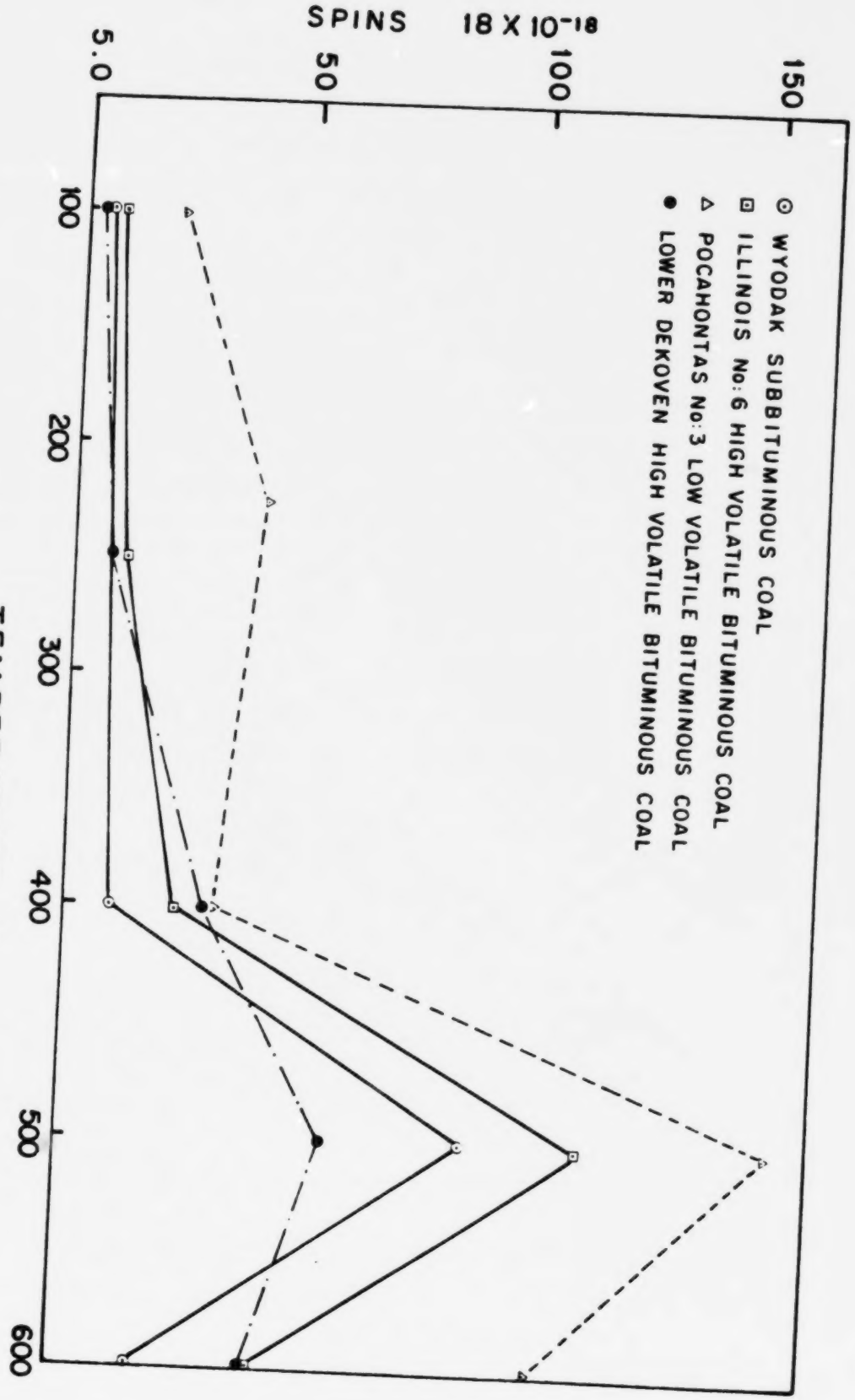
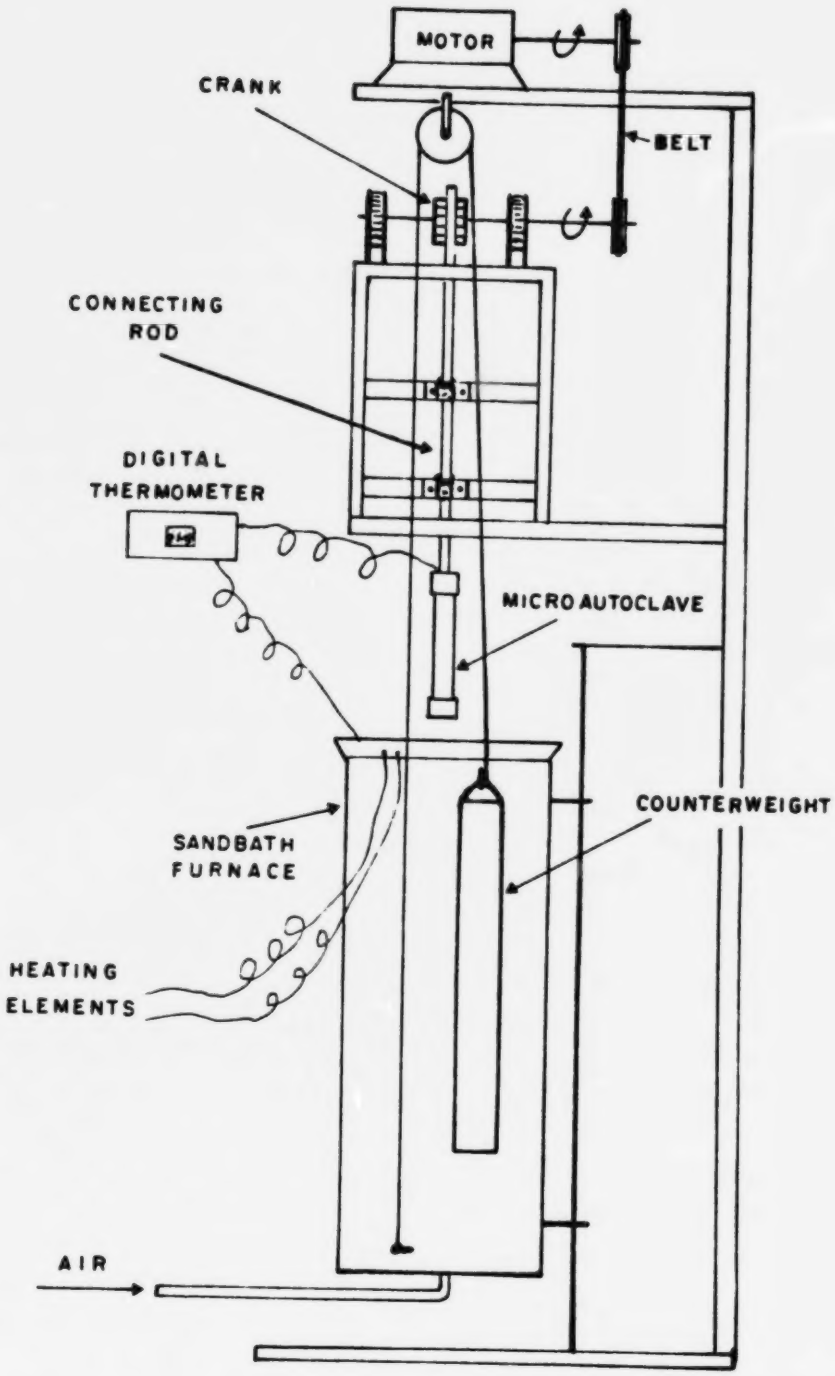


FIGURE 4: Free Radical Concentration vs. Temperature (Ref. 20)



MICROAUTOCLAVE UNIT

FIGURE 5: (Ref. 45)

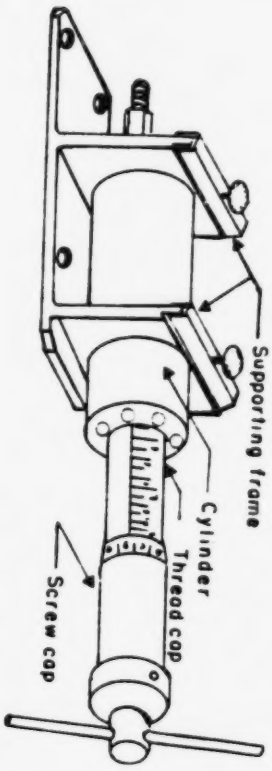


FIGURE 6: Coal Injector Used for Solvent Extraction (Ref. 37)

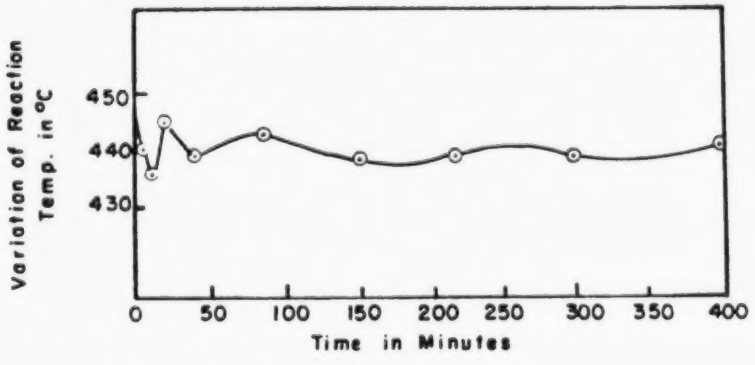


FIGURE 7: Variation of Temperature During Process of Solvent Extraction at 440°C in a Rapid Injection Autoclave System (Ref. 37)

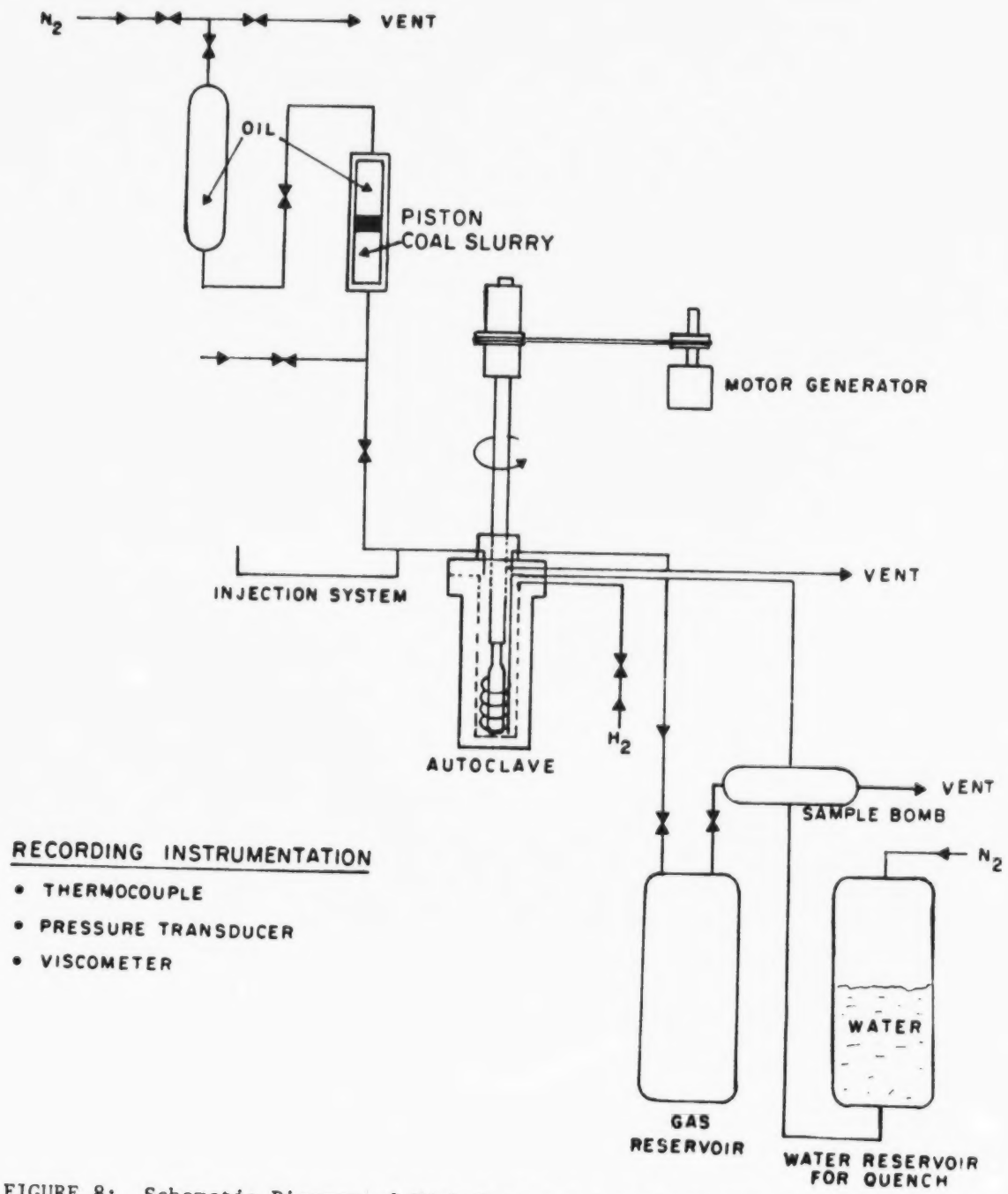


FIGURE 8: Schematic Diagram of High Pressure Autoclave with Pressurized Injection System (Ref. 41)

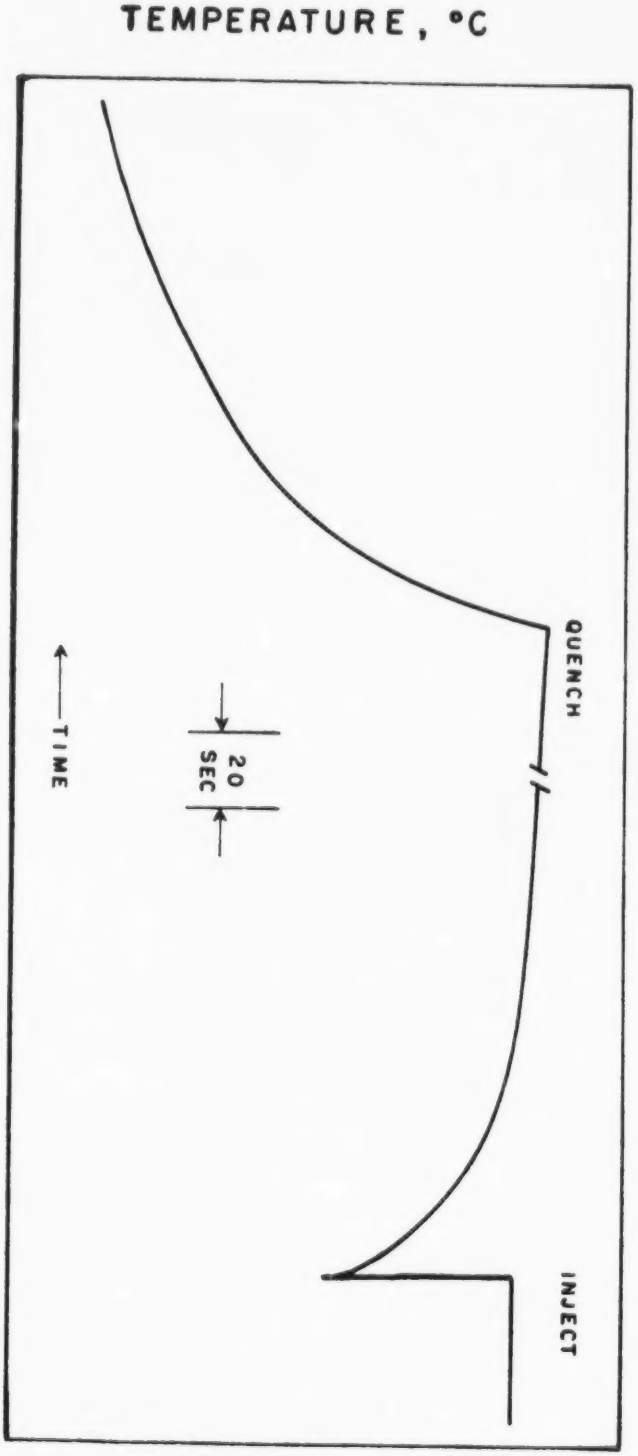
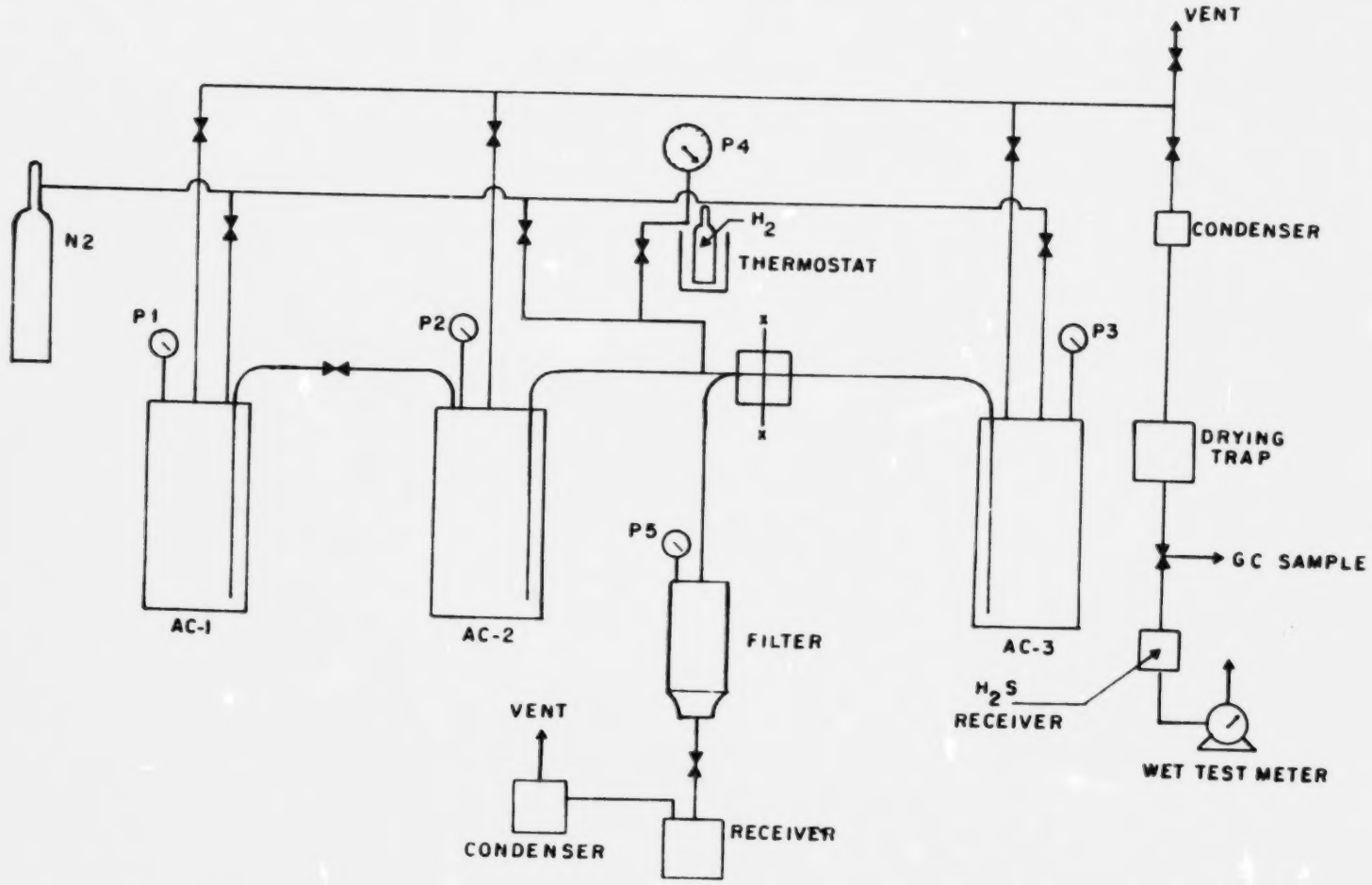


Figure: 9. TYPICAL TIME-TEMPERATURE PROFILE (Ref. 41)

Figure 10. SHORT RESIDENCE TIME COAL LIQUEFACTION APPARATUS - 3 AUTOCLAVES
(Ref. 30)



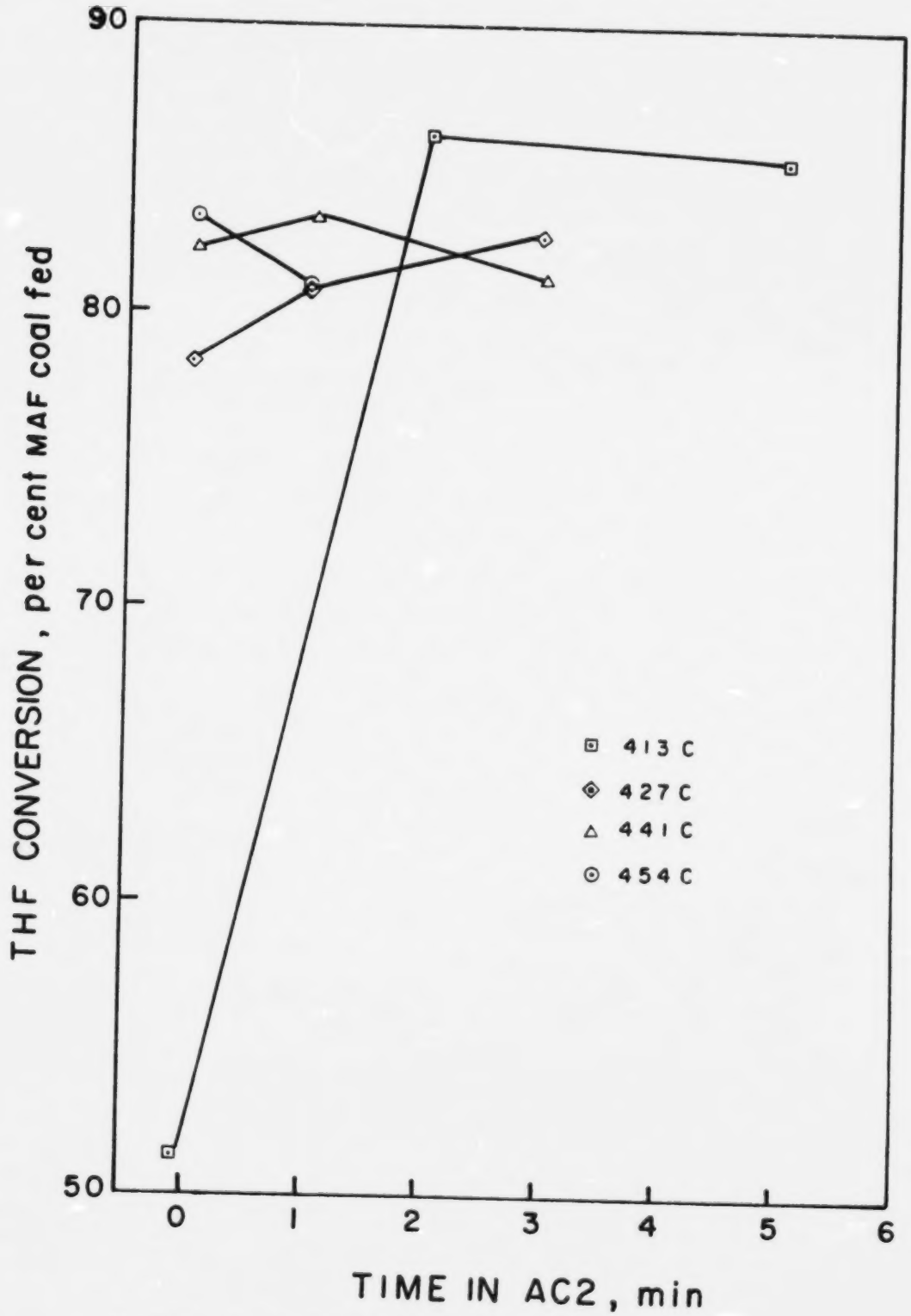


FIGURE 11: The Soluble Conversion vs. Time and Temperature (Ref. 30).

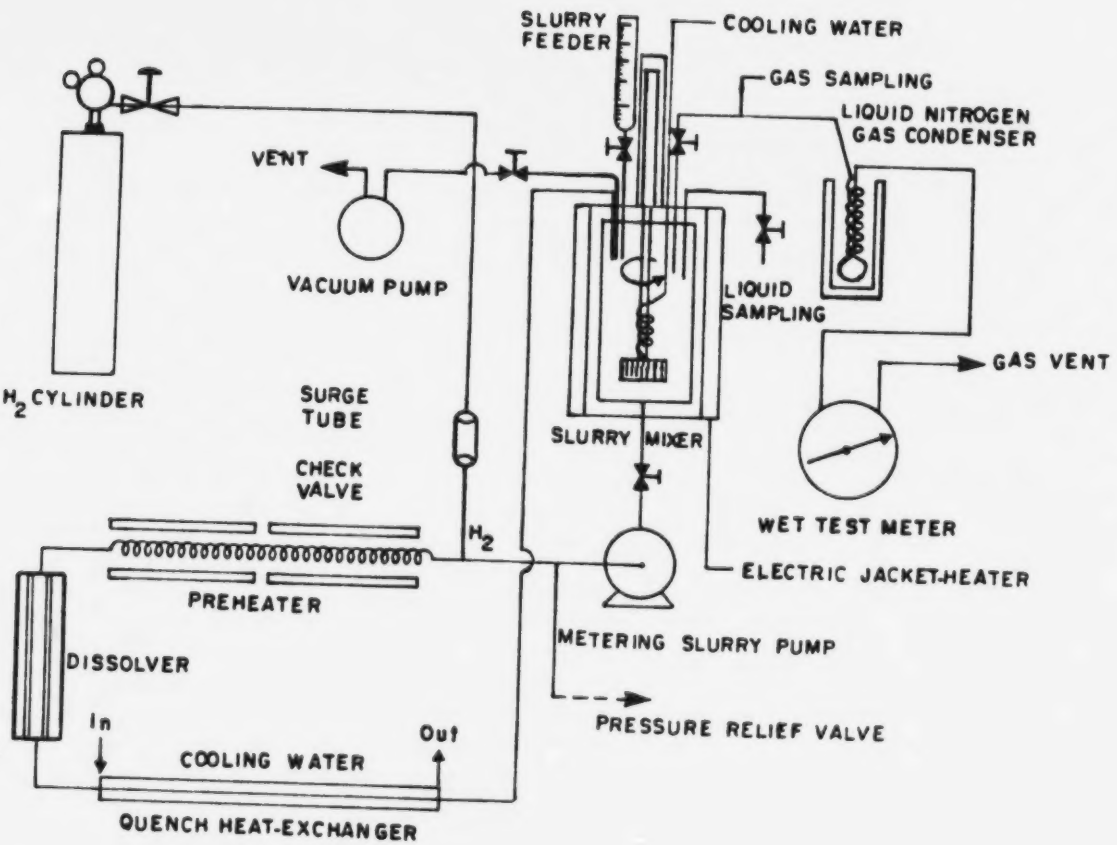
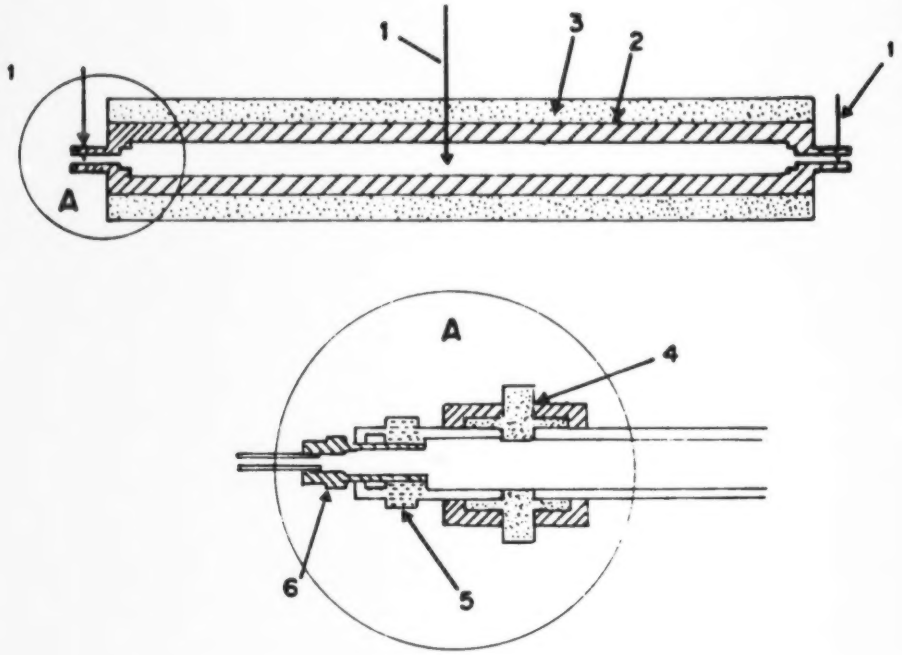


FIGURE 12: Batch Recycle System for Dissolution of Coal in a Hydrogen Donor Solvent (Ref. 48)



1- THERMO COUPLE

2- REACTOR TUBE 3/4" O.D. or 3/8" I.D. x 12"

3- ELECTRIC HEATER BLOCK

4- 3/4" UNION

5- 3/4" to 3/8" REDUCER

6- 3/8" to 1/8" REDUCER

FIGURE 13: Sectional View of Reactor (Ref. 48)

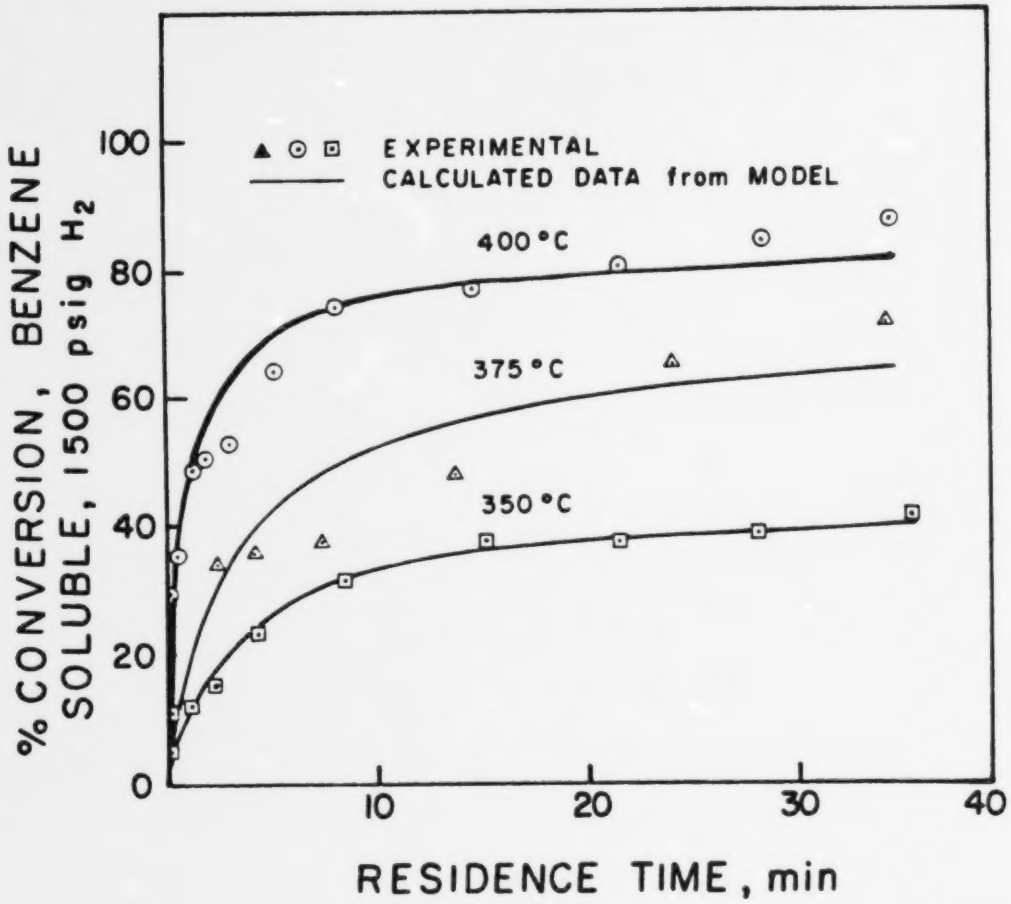


FIGURE 14: Kinetic Data and Fitness to a Hybrid Model Containing Both First and Second Order Terms, Hiawatha Coal (Ref. 48)

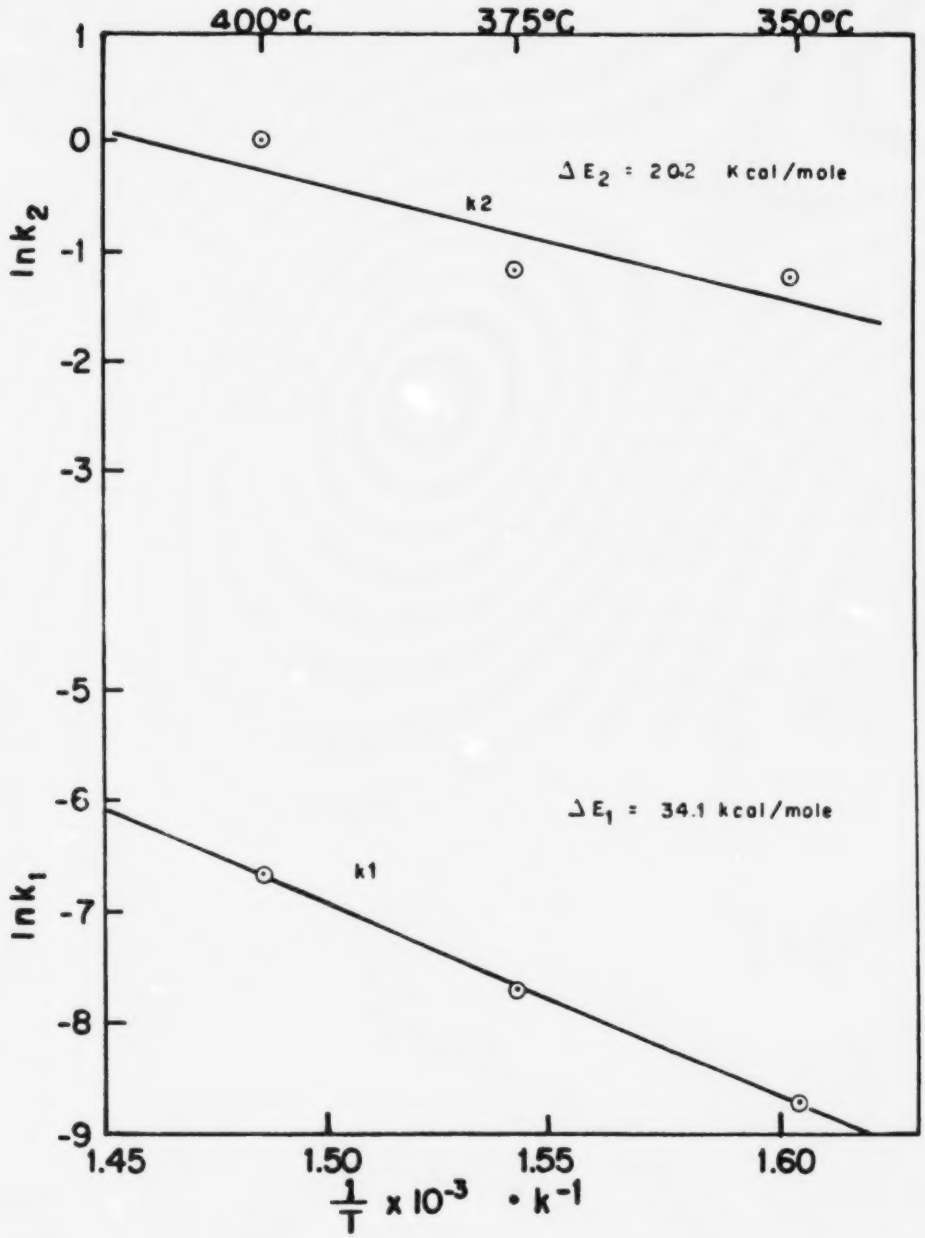


FIGURE 15: Arrhenius Plot (Ref. 48)